	Type	L #	Hits	Search Text	DBs
1	BRS	L1	0	bump near3 (Sn37Pb)	USPAT
2	BRS	L2	37	bump near3 (Sn adj2 Pb)	USPAT
3	BRS	L3	23	bump near3 (Sn adj2 Pb)	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB
4	BRS	L4	3	(copper adj2 (layer or film)) near10 (copper adj2 stud)	USPAT
5	BRS	L5	4383	cu adj2 cu	USPAT
6	BRS	L6	16	5 same blm	USPAT
7	BRS	L7	7166	cu adj2 cu	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB
8	BRS	L8	5	7 and blm	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB
9	BRS	L9	0	blm near10 NiV	USPAT
10	BRS	L10	0	blm same NiV	USPAT
11	BRS	L11	2	blm and NiV	USPAT
12	BRS	L12	4	blm and NiV	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB

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TITLE: Multilayered diffusion barrier structure for improving adhesion property

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A method has been provided for improving the adhesion of copper to a **nitrided metal** diffusion barrier material, such as TiN, in an integrated circuit substrate. The method provided a multilayered diffusion barrier structure, comprising a **nitrided metal** diffusion barrier layer and an oxy**-nitrided metal** layer. The formation of an oxy**-nitrided metal** layer, instead of an oxide layer, permits the optimization of both contact resistance
and adhesion property. The oxy**-nitrided metal** layer is formed either by the
partial incorporation of oxygen into the **nitrided metal** diffusion barrier or by
deposition in an oxygen ambient.

From thermodynamic arguments, good diffusion barriers for copper thus are
those that have a positive heat of formation with copper. The **nitrided metal**
diffusion barriers such as TiN, TaN, WN, TiSiN, TaSiN, WSiN, composed of mainly
nitrogen and other metallic components such as Ti, Ta, W, offer the best conductive diffusion barrier property against copper diffusion. Copper nitrides have positive heats of formation so that it is thermodynamically unfavorable for copper to bond to nitrogen. These nitrides are more

thermodynamically stable than copper nitrides and thus are effective against copper bonding and diffusion. Of all the mentioned nitrides, TiN and WN are similar to each other. TaN is a somewhat better barrier than either TiN or WN, and thus adhesion of CVD copper to TaN is much more difficult to achieve than to TiN or WN. The adhesion property of copper to an effective diffusion barrier however is poor.

To improve the adhesion of the **nitrided metal** diffusion barrier to copper, it is imperative to change the surface properties of the **nitrided metal** diffusion barrier layer. This surface should contain materials that bond with copper. Thermodynamically, it means that the compound from reactions of this material and copper should have a negative heat of formation, such as a copper oxide. One way to change the surface properties of the **nitrided metal** diffusion barrier thus is to form an oxy-nitride layer on the surface by oxy-nitriding the **nitrided metal** diffusion barrier layer surface, and the presence of oxygen in the oxy-nitride layer would promote the adhesion of copper to the diffusion barrier. The oxy-nitride layer comprises the metal, nitrogen, and oxygen, and serves to improve the adhesion of the multilayered diffusion barrier structure to the subsequently deposited layer. As oxygen is incorporated into the **nitrided metal** diffusion barrier surface, the surface becomes an oxy**-nitrided metal,** and no longer has the strong diffusion barrier property. This surface thus exhibits strong chemical bonding with the subsequent deposited layer. Furthermore, this thin oxy-nitrided layer is conductive and thus the contact resistance is reduced. The amount of oxygen in the oxy-nitride layer however has a strong affect on the contact resistance.

The oxidizing condition will produce an oxide layer, however thin, that raises the contact resistance because of its non conductive property. Care should be taken to avoid the extreme case of oxidizing the **nitrided metal** diffusion barrier that occurs by introducing an excessive amount of oxygen. One way to avoid over-oxidizing the **nitrided metal** barrier surface is to introduce a small amount of oxy-nitride contained gas or a precursor that contains oxygen and nitrogen to the barrier surface. The introduction of the oxy-nitride or oxygen-nitrogen combination reduces oxidizing of the surface. Therefore a method to improve the adhesion of the **nitrided metal** diffusion barrier without introducing a non-conductive oxide layer is to have a multilayer: a **nitrided metal** diffusion barrier layer to block foreign material diffusion, and a thin oxy**-nitrided metal** layer to provide the adhesion property. The oxygen content in this oxy-nitrided layer is small such that the **nitrided metal** layer is not oxidized and results in a non-conductive layer.

In the oxy-nitriding process, the metal comes from the **nitrided metal** diffusion barrier layer, oxygen comes from the ambient, and nitrogen can be from the **nitrided metal** diffusion barrier layer and the ambient. There are different ways of incorporating the metal, oxygen, nitrogen to form the oxy-nitride layer. One way is to introduce a small amount of oxygen to a thin surface of the **nitrided metal** diffusion barrier. To provide a thin oxy**-nitrided metal** layer such as TiON, TiSiON, TaON, TaSiON, WON, WSiON, the **nitrided metal** diffusion barrier surface is oxy-nitrided in an oxygen-contained ambient. The oxy**-nitrided metal** adhesion property improvement is most effective with TiN, a less effective diffusion barrier, and much less effective with TaN, a more effective diffusion barrier. This method uses the nitrogen

from the nitrided diffusion barrier layer. Another way is to introduce oxygen
and nitrogen from an ambient. Additional nitrogen thus comes from the ambient
source. Another way is to deposit a thin oxy-nitride metal diffusion barrier layer by using an oxygen/nitrogen precursor together with the precursors needed
to deposit the <u>nitrided metal</u> diffusion barrier. Not all oxy-nitrided materials however exhibit good adhesion property.

An improved method to improve adhesion is to form a multilayer: a <u>nitrided</u>
<u>metal</u> diffusion barrier layer and a thin oxy-nitride metal layer. The thin oxy-nitride metal layer comprises the metal, nitrogen, and oxygen, hence the name oxy-nitride metal, the oxygen species being less than the nitrogen species, that works best since it is much more conductive than an oxide, and the adhesion property does not differ significantly.

Accordingly, a method to improve the adhesion property of copper to the <u>nitrided metal</u> diffusion barriers such as TiN, TiSiN, TaN, TaSiN, WN, WSiN, by
forming a multilayered diffusion barrier structure is provided. The provided
multilayered diffusion barrier is deposited on an underlayer, and provides improved adhesion to a subsequently deposited layer. The method comprises the
steps of: a) Depositing a <u>nitrided metal</u> diffusion barrier layer on the underlayer in a diffusion barrier deposition equipment, whereby this diffusion
barrier layer serves as a barrier between the underlayer and the subsequently
deposited layer; b) Forming a thin metal nitrogen-rich oxy-nitride layer by oxy-nitriding the diffusion barrier material surface, this oxy-nitride layer comprises the metal, nitrogen, and oxygen, the oxygen species being less than
the nitrogen species, whereby this layer serves to improve the adhesion of

the
multilayered diffusion barrier structure to the subsequently deposited layer.

The two layers: **nitrided metal** diffusion barrier layer and the oxy-**nitrided metal** layer are formed in sequence. The method includes the formation of these two layers in two separate locations: two process chambers in the same process equipment, or in two separate process equipment. The formation of the **nitrided metal** diffusion barrier will occur in the first process chamber (of the two chamber equipment), or in the first process equipment. The substrate will then be moved to the second process chamber (of the two chamber equipment), or to the second process equipment for the oxy-nitriding process. The oxy-nitriding process to form the oxy-**nitrided metal** layer will require an oxygen-contained ambient. In some aspects of the invention, an elevated temperature is also provided. The elevated temperature ranges from 200.degree. C. to 1200.degree. C., with 300-500.degree. C. being a typical temperature range. The oxy-nitriding time ranges from a few seconds to several minutes, depending on many factors such as the optimization of process flow, the optimization of the desired level of adhesion, the optimization of contact resistance, etc.

In some aspects of the invention, the **nitrided metal** diffusion barrier is selected from a group consisting of TiN, TiSiN, TaN, TaSiN, WN, WSiN.

The method also provides the thickness of the oxy-nitride layer on the surface of **nitrided metal** diffusion barrier to be less than 5 nm. The 5 nm

thick or less metal oxy-nitride layer offers adequate adhesion, and does not increase much the overall thickness of the multilayered diffusion barrier structure. Some applications, such as the ones in advanced semiconductor processing, require that the overall diffusion barrier thickness to be less than 50 nm, so a thin metal oxy-nitride layer is desirable, provided that adequate adhesion is achieved.

The method also provides various techniques to deposit the **nitrided metal** diffusion barrier. The evaporation technique can deliver the **nitrided metal** diffusion barrier by heating the source material. The sputtering technique can
deliver the **nitrided metal** diffusion barrier by sputtering a target in a nitrogen-contained ambient. TiN diffusion barrier can be formed using a Ti target. Or by using a TiN target, the sputtering technique can deliver TiN without the need for the additional nitrogen ambient. The sputtering technique
however does not fill the gap very well. The chemical vapor deposition technique can deliver the **nitrided metal** diffusion barrier by using appropriate
precursors. Typical TiN liquid precursors are tetrakisdimethylaminetitanium (TDMAT), tetrakisdiethylaminetitanium (TDEAT), and tetrakismethylethylaminetitanium (TMEAT). These precursors can be combined
with a nitrogen source such as ammonia (NH.sub.3), or nitrogen. Typical TaN liquid precursors include pentadiethylaminetantalum (PDMAT), that can be used
with or without a nitrogen source. Typical WN chemical vapor deposition uses a
precursor such as WF.sub.6 with nitrogen. The addition of other materials such
as silicon can produce ternary **nitrided metal** diffusion barriers such as TiSiN,
TaSiN, or WSiN. To further excite the precursors, additional energies from a
plasma source can be added as in the technique of plasma-enhanced chemical vapor deposition.

The method also provides various oxygen-contained ambient. To provide a thin oxy-**nitrided metal** layer, an ambient comprising the oxygen species is needed. The oxygen species can be oxygen gas, N.sub.2 O, NO.sub.2 gas, water
vapor, alcohol vapor, OH ligand, chemicals containing OH ligand, chemicals releasing OH ligand upon high temperature annealing. The oxygen species can
also be diluted in other gases.

The method also provides the reactive oxygen species by plasma source to oxy-nitriding the **nitrided metal** diffusion barrier layer. The plasma source can be a direct plasma source or a downstream plasma source. In some aspects
of the invention, the **nitrided metal** diffusion barrier is deposited by plasma-enhanced chemical vapor deposition. In this case, the underlayer is exposed to plasma energies of the diffusion barrier precursors. At the end of
the deposition, the diffusion barrier precursors are turned off, and an oxygen-contained ambient is introduced. The presence of the oxygen plasma will
incorporate some oxygen into the **nitrided metal** diffusion barrier to form the
metal oxy-nitride metal layer. As mentioned earlier, care should be taken to avoid oxidizing the **nitrided metal** diffusion barrier.

The method also provides an alternate way to oxy-nitriding the **nitrided metal** diffusion barrier layer. In the case of the high temperature **nitrided metal** diffusion barrier deposition process, the oxy-nitriding process occurs during the cooling down period of the diffusion barrier formation. The oxy-nitriding process is then independent of time, i.e. self-limiting, and requires no external heating source, i.e. self-annealing process. A preferred method to achieve this process is to move quickly the deposited hot **nitrided metal** diffusion barrier to an oxygen-contained ambient where the **nitrided metal**
diffusion barrier is annealed in an oxygen-contained ambient by its own

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